

Results of Studies Correlating Total Organic Chlorine  
and Dioxin/furans in Selected Oregon Sediments

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Introduction

1. In august 1990 EPA, Region X, requested that USACE, Portland District, test some previously collected sediment samples, which had been analyzed for dioxins, for total organic chlorine (TOCL). Funding of the study came from EPA. The idea was to determine if there was a strong enough correlation between sediment concentrations of organochlorines (TOCL) and dioxins to use the much cheaper TOCL analysis as an indicator of potential dioxin contamination. The cost of a TOCL analysis was \$150.00 per sample while that of dioxin analysis was around \$1300.00 per sample.

Methods

2. Thirty four sediment samples were now tested for TOCL. These samples came from the Columbia, Chetco and Willamette Rivers and Yaquina Bay (see maps for locations). The samples had been maintained frozen at Battelle, Pacific Northwest Division, Marine Sciences Lab, Sequim, WA. They were sent to the University of Illinois where 10 gram samples were tested for TOCL by neutron activation analysis. The method consists of extracting organochlorines from about 10 grams of wet sediment with hexane and dry sodium sulfate then evaporating the hexane in a plastic vial. Neutron activation analysis involves bombarding the samples with neutrons then measuring the resultant radioisotopes of the chlorine atoms (the bromine content of the samples was also determined).

3. There are three commonly used measures of organochlorines - AOX, EOCL and TOCL. AOX is the adsorbable organic chlorines which attach to fine-grained, colloidal material in water and sediment. EOCL is extractable organic chlorine of molecular weight of 1,000 or less. TOCL is total organic chlorine of molecular weight of 10,000 or less. TOCL was chosen in this study in order to measure as much of the organochlorine as possible. The method used by University of Illinois for measuring TOCL by neutron activation analysis was recommended by Battelle.

4. As a quality assurance measure two standard reference sediments, obtained from the National Research Council of Canada, were included as samples. The reference sediments were certified for their polychlorinated biphenyls (PCBs) content. Quality control was established by measuring the TOCL in four procedural blanks. In this procedure every step was carried out as if there were sediment in the sample. The result is a measure of the TOCL

in the hexane, sodium sulfate and plastic of the vials which is then subtracted from the sample results to obtain the TOCL attributable to the sample sediments.

## Results/discussion

### Quality control

5. The raw data from the procedural blanks and Canadian reference sediments are shown in the appendix in Table A. The mean chlorine value from the 4 procedural blanks was subtracted from the sediment values to obtain concentrations corrected for blank. The detection limit was determined by using the standard deviation of the procedural blanks. This was done by dividing the standard deviation by 10 to obtain a per gram detection limit of 31.6 ppb. Sediment samples with a TOCL of 30 ppb or less were considered below the detection limit and not used in data analysis.

6. The method accurately reflected the concentrations of chlorine in the reference sediments. The Canadian reference sediments were certified for 22 and 112 ppb of PCBs respectively. The method yielded 288 and 668 ppb TOCL for the reference sediments, indicating another source of organochlorines in them, but reflecting the trend towards increased PCBs in reference material.

### Data patterns and analysis

7. Table 1 shows the raw data from 15 of the 34 samples. Only 15 sediment samples were included in Table 1 because they had values for TOCL and dioxins that were above detection limits. The raw data for the other 19 samples is in the enclosed appendix. These 19 samples were excluded from Table 1 because they were below TOCL detection limits or were not analyzed for dioxin/furans.

8. Table 1 presents four sediment samples from the Columbia River (CR), nine from the Willamette River (WR) and two from Yaquina Bay (YQ) (see maps). The samples ranged from 0.4 to 92.1 percent fines (silt/clay). The total organic carbon (TOC) content ranged from 0.2 to 7.5 mg/g. Grain size of sediment particles varied from 0.020 to 0.440 mm (medium silt to medium sand).

9. TOCL values were highest in Willamette River sediments followed by Chetco, Yaquina Bay and Columbia River in that order. The Willamette River samples showed TOCL levels ranging from 115 to 2380 ppb. WR-GC-3A&B and WR-GC-4, the two samples with highest TOCL, were taken from areas in Portland Harbor where high levels of contaminants had been found before - the Doan Lake area and downstream from McCormick & Baxters. Willamette River samples were also highest in total dioxin/furans (mean 5.4 ppb, range 0.9 - 19.0 ppb).

10. Most of the Columbia River samples were at or near the detection limit for TOCL (30 ppb). Of 15 Columbia River samples only 4 were above the detection limit for TOCL. These 4 were included in Table 1. Two of the four samples were just above the TOCL detection limit (CR-GC-6A AND CR-GC-25). CR-VC-12A&B (TOCL = 217 ppb) was taken at the mouth of the Westport slough Columbia River mile 43+05 and CR-GC-24 (TOCL = 90 ppb) was taken at St. Helens (RM 85+45) about 3/4 mile from the outfall of the Boise Cascade pulp mill. The TOCL for these two samples was in the range of the low end of TOCL values for Willamette River samples and about equal to the TOCL values for Yaquina Bay samples. The Columbia River samples that were below detection limits for TOCL came from regularly dredged channel areas which are usually coarse sand free of contaminants. A few samples (CR-GC-2,5,6) came from high fines areas near Longview (RM 63-64).

11. Two of three Yaquina Bay samples were above the TOCL detection limit and are included in Table 1. The TOCL and dioxin concentrations were intermediate between Columbia and Willamette River values. The Yaquina Bay samples were from boat harbor areas.

12. Chetco River samples were next highest in TOCL to Willamette River samples (mean 272 ppb, range 58-596 ppb). Unfortunately these samples were not analyzed for dioxins, two samples are archived in cold storage at Battelle.

13. No correlation between bromine and chlorine was observed in the sediment samples. Although bromine is another halide in the same chemical group as chlorine it is not as much a constituent of organic compounds as chlorine. The bromine concentrations found in the Chetco River samples were 2 to 3 times higher than Columbia, Willamette River and Yaquina Bay samples.

14. There are multiple sources of dioxin/furans in the Columbia River, including atmospheric, and no one has yet worked out the contribution of each to the sediment load. Interestingly, the pattern of average concentrations of total dioxin/furan congeners in the Columbia River samples is similar to that of the sediment in Lake Siskiwit, a land-locked wilderness lake on an island in Lake Superior (compare figures A and B in the appendix)(3). The origin of the dioxin/furans in Lake Siskiwit sediment is considered to be totally atmospheric (2).

#### TOCL - dioxins correlation

15. Figure 1 is a scatter plot showing the relationship between TOCL and dioxins/furans in the 15 sediment samples. There was a significant correlation between the two ( $R=0.712$ ,  $p<0.02$ ,  $n=15$ ). However, the usefulness of this correlation is unclear, especially in the context of using TOCL as a predictor of dioxin contamination in non point source sediment samples. The problem is that only a

very small fraction of the TOCL was contributed by dioxins. This can be calculated assuming that most of the dioxin/furan congeners in the samples were in the OCDD category which contains 8 chlorine atoms per molecule. The contribution of the chlorines to the OCDD molecular weight is about 60 percent. For example, in sample WR-GC-3A&B the sample with the highest total dioxins/furans, the amount of chlorine in the sample is 11.4 ppb (19 ppb dioxin/furans X 60 % Cl). Dividing the 11.4 ppb chlorine from dioxins/furans by the 1665 ppb TOCL gives 0.68% of the TOCL contributed by chlorine from dioxins/furans. In other words, 99.32 % of the TOCL was contributed by sources of organochlorines other than dioxin/furans. The average contribution of chlorine attributed to dioxin/furans to the TOCL in the 15 samples in Table 1 is 0.58% (ie. 99.42 % of Cl from non dioxin sources). Therefore a high TOCL in these sediment samples is not necessarily an indication of dioxin/furan contamination, despite the correlation between TOCL and dioxins/furans, since the dioxin/furans levels might be exceedingly low. Alternatively, one can also envision a situation where a sediment sample contained a environmentally significant concentration of dioxins/furans and a low TOCL. In this case, if TOCL was used as an indicator, dioxin/furan contamination might not be revealed. A high TOCL still could be used as an indicator that further analysis of sediment samples in an area may be needed since the sediments may be contaminated by other organochlorines not attributable to dioxin/furans.

16. Other sources of organochlorine in sediment may be pesticides, PCBs, chlorophenols, plastics or other semivolatiles. These probably make up most of organochlorines in the sediment samples although there may be other unknown organochlorines that contribute to the TOCL. A more exact accounting of the contribution of the above to the TOCL is needed. The data from this study is insufficient for this purpose since we did not measure other sources of organochlorine. A Swedish study of extractable organochlorine (EOCL) suggested that less than 1% of EOCL could be identified as dioxin/furans, DDTs, PCBs, toxaphenes and chlorophenols (2). The rest was unidentified and could be a potential hazard.

17. As mentioned earlier the Chetco River samples were not analyzed for dioxin/furans. However, the data may still be useful because the correlation between TOCL and dioxins would predict that Chetco dioxin/furans are intermediate between Willamette and Columbia River values. The regression line from figure 1 predicts roughly 2.4 ppb dioxin/furans in the Chetco River samples. It would be interesting to test this hypothesis by analyzing the archived Chetco samples.

#### Usefulness of TOCL

18. The best use of TOCL would be as a tool to help map contamination from a known source of dioxins as was done in a

Swedish study of correlations between extractable organic chlorine (EOCL) and dioxin congeners in coastal sediments outside a pulp mill in the Iggesund area (1). In the Swedish study the dioxin/furans only accounted for a small fraction of the EOCL (about 1/100,00) yet the contamination could be easily mapped seaward from the pulp mill. Our results are similar with the average dioxin/furans contribution to TOCL being about 1/1,000 (ranging from approx. 6/100,000 to 2/100, mean=1/1,000). Interestingly, the Swedish study found concentrations of EOCL at least 40 times higher than the TOCL found in the sediments reported here. The reason for this difference is unknown. At any rate, TOCL could serve as a useful and cheap mapping tool for point source contamination. The cost of a TOCL analysis is approximately \$150.00 vs a dioxin analysis of \$1,300.00 so the savings in costs of mapping a site would be substantial (about 90 %).

19. As a mapping tool TOCL seems to work in a coastal sediment system, as in the Swedish study, where the sediments are not very mobile. But, its effectiveness in a faster moving riverine environment needs to be proven. Here, the effluent may be composed of dioxin/furans in solution or adsorbed to fine particles or colloidal material which may wash far downstream before settling out into the sediment. In a riverine system, like the Columbia River, where a dam may be downstream from a point source and where sediments tend to collect behind and upstream from the dam, mapping may be useful. A comparison of sediments upstream and downstream from the dam could show the extent to which dioxin/furans are trapped upstream from the dam.

### Conclusions

20. There is a positive, significant correlation ( $R=0.71$ ,  $p<0.02$ ,  $n=15$ ) between the concentration of TOCL and dioxins/furans in the samples studied. Even though there is a correlation between TOCL and dioxin/furans the best use of TOCL is as a mapping tool for known point source contamination rather than as a tool to look for dioxin/furan contamination in non point source areas. This is because over 99% of the TOCL came from other sources, presumably pesticides, PCBs, Chlorophenols, other chlorinated semivolatiles and plastics or other unknown sources, with dioxin/furans contributing less than 1 %. Thus, a high TOCL may or may not indicate dioxin contamination but may be presumed to signal a potential problem with other organochlorine contaminants. A low TOCL may not reveal an underlying problem with dioxin/furan contamination.

21. TOCL may be a cost effective means of mapping point sources of dioxin/furans, reducing costs by about 90%.

22. The Willamette river sediments in Portland Harbor showed the highest TOCLs and dioxin/furans. Columbia River sediment samples were, for the most part, at or below the TOCL detection limit.

This is probably because most of the samples came from regularly dredged channel areas which are low in contaminants. Only 3 of 15 Columbia River samples were above detection limit levels for TOCL. There was no evident pattern of TOCL or dioxin/furans in Columbia River samples associated with potential sources of organochlorine such as pulp mills. For instance, two Columbia River samples taken downstream from the outfalls of the Wauna and James River mills were near the detection limit for TOCL and low in total dioxin/furans (bottom third of 27 samples where dioxin/furans were measured).

23. Further TOCL/dioxin studies, especially of sediments high in fines and total organic carbon where dioxin/furans concentrate, are needed to determine the usefulness of TOCL in predicting dioxin/furans or other organochlorine contamination. Point sources of dioxins/furans need investigation to see if the TOCL is an effective, cost effective mapping tool. The contribution of other organochlorines, some of which may potentially be hazardous, to the TOCL needs further elucidation.

Table 1. Concentrations of total organic chlorine (TOCL), bromine (Br), and dioxins; percent fines and total organic carbon (TOC) in sediment samples from Columbia (CR) and Willamette Rivers (WR) and Yaquina Bay (YQ).

Sample	TOCL	Br	Dioxins*	Fines	TOC
		ppb		%	mg/g
CR-GC-6A	31	<3.0	0.11	92.1	7.50
CR-GC-24	90	6.8	0.01	0.4	1.10
CR-GC-25	32	3.9	0.05	0.5	<0.20
CR-VC-12A&B	217	<3.0	0.30	79.0	0.84
WR-GC-2	610	5.5	4.10	78.3	2.40
WR-GC-3A&B	1665	12.5	19.00	87.9	4.00
WR-GC-4	2380	13.0	6.30	88.4	2.80
WR-GC-5	424	10.0	7.50	67.0	2.00
WR-GC-6	161	5.2	2.10	63.3	1.40
WR-GC-7	283	15.0	1.90	70.3	2.50
WR-GC-8	137	6.1	0.90	19.6	0.90
WR-GC-9	115	5.8	5.00	55.5	2.60
WR-GC-10	286	13.0	1.80	76.1	3.10
YQEPA-8	230	31.0	0.58	21.7	1.33
YQEPA-9	78	17.0	0.95	69.9	2.40

\* Total concentration of dioxin and furan congeners.

Out of 34 samples, the above 15 represent data in which the TOCL was above the detection limit. Eleven Columbia River samples and one Yaquina Bay sample were not included in the table because TOCL was below detection limit. No dioxin/furan analyses were conducted on the six Chetco River samples. The TOCL for sample WR-GC-3A&B is the average of duplicate samples (WR-GC-3A and 3B). The raw data for all 34 samples is in the appendix.



#### REFERENCES

1. Jonsson P., Rappe C., Kjeller L., Hakanson L. and Jonsson B. Report from joint study financed by the National Swedish Environmental Protection Board titled " Polychlorinated dibenzop-dioxins (PCDDs), dibenzofurans (PCDFs) and extractable organic chlorine (EOCL) in coastal sediments outside a pulp mill".
2. Hutzinger O., Blumich M. Sources and fate of PCDDs: an overview. Chemosphere, vol. 13, No. 6/7, pp 581-600, 1985.
3. Smith R., O'Keefe P., Aldous K., Valente H., Connor S., and Donnelly R. Chlorinated dibenzofurans and dioxins in atmospheric samples from cities in New York. Environ. Sci. Technol., 24, 1502-1506, 1990.

Table A.

CONCENTRATIONS OF ORGANIC CHLORINE  
AND ORGANIC BROMINE IN SEDIMENT

$\mu\text{g/Kg}$  (dry weight)

MSL Code	Sample No.	Cl	Br	PCB	Dioxin
18	CR-GC-2B, Rep. 1	< 30	< 3	--	0.15
22	CR-GC-2B, Rep. 2	< 30	< 3	--	--
28	CR-GC-4	< 30	5.0	--	0.04
7	CR-GC-5	< 30	< 3	--	0.02
45	CR-GC-6A	31	< 3	--	0.11 composite 6A + 6B
37	CR-GC-6B	< 30	< 3	--	0.11 composite 6A + 6B
10	CR-GC-15	< 30	11	--	0.04
38	CR-GC-16	< 30	17	--	0.04
5	CR-GC-17	< 30	7.4	--	0.07 composite 17 + 18
13	CR-GC-18	< 30	7.6	--	0.07 composite 17 + 18
12	CR-GC-23	< 30	7.1	--	0.01 composite 23 + 24
9	CR-GC-24	90	6.8	--	0.01 composite 23 + 24
46	CR-GC-25	32	3.9	--	0.05 composite 25 + 26
40	CR-GC-26	< 30	6.2	--	0.05 composite 25 + 26
33	CR-VC-12A&B	217	< 3	< 50	0.3
8	WR-GC-2	610	5.5	--	4.1
11	WR-GC-3A	1780	12	--	19 composite 3A + 3B
47	WR-GC-3B	1550	13	--	19 composite 3A + 3B
17	WR-GC-4	2380	13	--	6.3
4	WR-GC-5	424	10	--	7.5
3	WR-GC-6	161	5.2	--	2.1
6	WR-GC-7	283	15	--	1.9
31	WR-GC-8	137	6.1	--	0.9
15	WR-GC-9	115	5.8	--	5.0
35	WR-GC-10	286	13	--	1.8
44	YQEPA-6	< 30	5.7	< 80	0.27
20	YQEPA-8	230	31	< 80	0.58
43	YQEPA-9	78	17	< 120	0.95
19	CHR-P-1	596	46	--	--
26	CHR-P-2	58	59	--	--
41	CHR-P-3	127	16	--	--
4	CHR-P-4	352	8.5	--	--
42	CHR-P-5	227	26	--	--
16	CHR-P-8	< 30	7.9	--	--

-- = data not available

Table A cont'd.

CONCENTRATION OF ORGANIC CHLORINE  
AND ORGANIC BROMINE IN SEDIMENT (continued)

<u>MSL Code</u>	<u>Sample No.</u>	<u>Cl</u> <u>ng/Vial</u>	<u>Br</u>	
1	Proc. Blank 1	897	26	
30	Proc. Blank 2	1230	26	
34	Proc. Blank 3	1598	40	
36	Proc. Blank 4	1510	31	
Mean $\pm$ SD		1309 $\pm$ 316	31 $\pm$ 7	
		<u><math>\mu</math>g/Kg</u>		
25	CRM HS-1	288	81	Certified 22 $\mu$ g/kg PCB
21	CRM HS-2	668	91	Certified 112 $\mu$ g/kg PCB



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Marine Analytical  
Chemistry Standards  
Program

Programme de standards  
de chimie analytique  
marine

## CS-1, HS-1, HS-2

### Marine Sediment Reference Materials for Polychlorinated Biphenyls

CS-1, HS-1 and HS-2 are natural marine sediment research materials for determinations of polychlorinated biphenyls (PCB). CS-1 is a coastal sediment collected in the Laurentian Channel midway between Nova Scotia and Newfoundland, and the two sediments, HS-1 and HS-2, were collected from Nova Scotian harbours.

This suite of samples provides a range of PCB levels from below 2 ppb in CS-1 to 112 ppb in HS-2. The matrix varies from a clean carbonaceous clay to an organic and sulfur rich material from a commercially active harbour.

The materials have been freeze dried, homogenized in a modified cement mixer and sub-sampled into solvent-rinsed pint-sized steel cans. Each can contains about 200 grams of material.

To order these materials, or for further technical information, contact:

Marine Analytical Chemistry Standards Program  
National Research Council of Canada  
Atlantic Research Laboratory  
1411 Oxford Street  
Halifax, Nova Scotia, Canada B3H 3Z1  
Telephone (902) 426-8280  
Facsimile (902) 426-9413  
Telex 019-21653

Determinations have been carried out on CS-1, HS-1 and HS-2 using packed column gas chromatography and electron capture detection. Aroclor 1254 has been used as the standard PCB mixture. The results ( $\mu\text{g}$  PCB/kg dried sediment) are summarized below:

CS-1	1.15	$\pm 0.60$	$\mu\text{g/kg}$
HS-1	21.8	$\pm 1.1$	$\mu\text{g/kg}$
HS-2	111.8	$\pm 2.5$	$\mu\text{g/kg}$

Uncertainties are expressed as  $\pm$  one standard deviation for results based on a minimum of 32 extractions of each sediment.

Homogeneity tests and determinations of PCB in CS-1, HS-1 and HS-2 were carried out using 35 gram samples of sediments.

Typical data from capillary column gas chromatography using electron capture detection for HS-1 and HS-2, will be supplied with the marine sediments. Quantitative data for individual PCB compounds are as follows:

HS-1 and HS-2, will be supplied with the marine sediments. Quantitative data for individual PCB compounds are as follows:

Polychlorinated Biphenyl Concentrations (micrograms/kilogram of dry sediment)		
IUPAC#	HS-1	HS-2
101	1.62 ± 0.21	5.42 ± 0.34
138	1.98 ± 0.28	6.92 ± 0.52
151	0.48 ± 0.08	1.37 ± 0.07
153	2.27 ± 0.28	6.15 ± 0.67
170	0.27 ± 0.05	1.07 ± 0.15
180	1.17 ± 0.15	3.70 ± 0.33
194	0.23 ± 0.04	0.61 ± 0.07
196	0.45 ± 0.04	1.13 ± 0.12
201	0.57 ± 0.07	1.39 ± 0.09
209	0.33 ± 0.10	0.90 ± 0.14

Figure A. Average dioxin/furan concentration in lower Columbia River sediment. The values are the averages, for all the sediment samples, of total concentrations in each congener class.

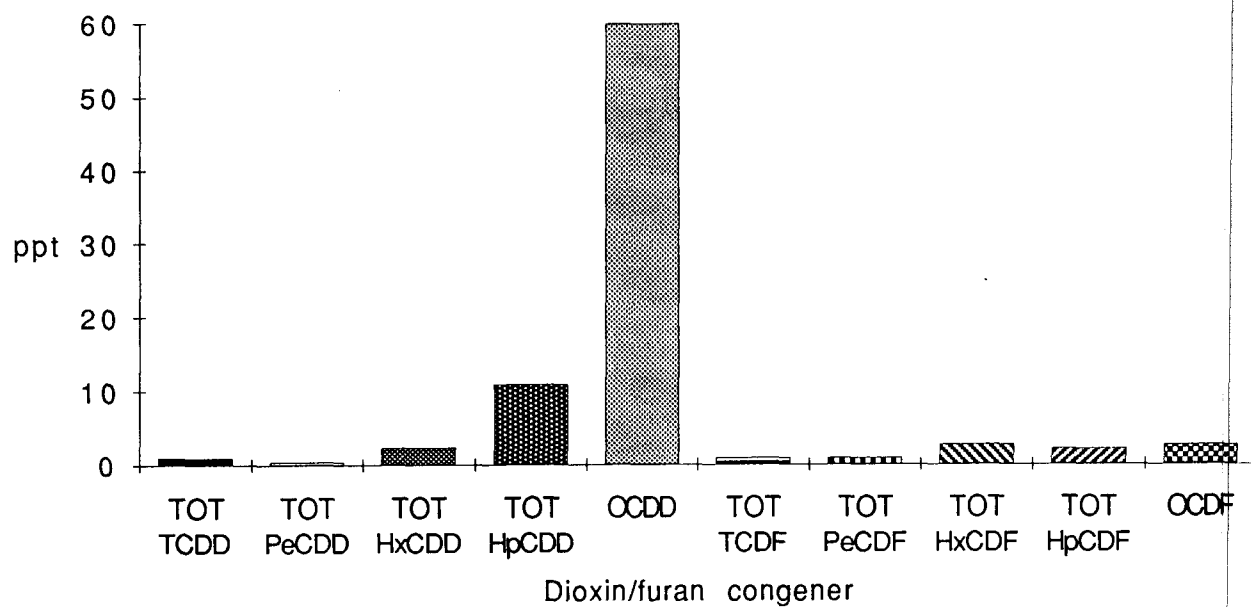


Figure B. Dioxin/furan concentrations in Lake Siskiwit sediment.  
Explanation is same as for figure A.

